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Distribution of Th-232 and Th-228 in Santos and São Vicente Estuary, São Paulo, Brazil

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Abstract

In the last decades considerable attention has been given to technologically enhanced natural occurring radioactive material (TENORM). Within this frame, of particular concern is the phosphate fertilizer industry. Santos Basin, located in Southwest Brazil, São Paulo State, comprising Santos and São Vicente estuarine system, is considered the most important industrial region of the country. Among the industrial activities present, phosphate fertilizer plants are responsible for the production of 69 millions tons of phosphogypsum waste, which is stockpiled in the surrounding environment. This waste concentrates radionuclides of the natural series originally present in the phosphate rock used as raw material. This study aims to evaluate the environmental impact of such activities in the sediments of the estuarine system. ^{232}Th and ^{228}Th concentrations in Santos and São Vicente estuary sediments were determined by neutron activation analysis and gamma spectrometry, respectively. ^{232}Th concentration ranged from 6.5 to 198 Bq kg^{-1}, with mean value of 57±39 Bq kg^{-1}, for 42 samples. ^{228}Th content varied from 12 to 110 Bq kg^{-1}, with a mean value of 74±23 Bq kg^{-1}, for 18 samples. It can be seen that the amount of ^{232}Th is higher in the rivers close to the phosphogypsum piles, at least five points were identified as being affected by anthropogenic factor.

1. INTRODUCTION

Thorium is an element quite insoluble in environmental conditions. Its geochemistry is basically defined by its unique valence state (4+) and low size of the ion that promote intense interaction with water and others substances forming complex ions. In solution Th precipitate rapidly due to the very low solubility product of $Th(OH)_4$ of approximately 10^{-35} [1]. The ^{232}Th content in river and near shore sediments is almost always related to weathered or detrital material, associated with heavy minerals, that formed the sediments, reflecting the local mineralogy, while ^{228}Th have an authigenic origin due to the short half-live of its parent ^{228}Ra (5.75 yr).

Human activities also contribute to the elemental composition of sediments and in some situations, give rise to the total amount of a particular element, as in the case of technologically enhanced natural occurring radioactive materials (TENORM). The contamination of land and sediments by TENORM is of major concern [2, 3, 4, 5, 6].

Measurement of radionuclides concentration along river-estuary-ocean transects has been used to obtain information on the weathering process, transport mechanism, and geochemistry from land to sea, as well as, identify pollution sources. Once man-made activities have the potential to highly affect the composition of the sediments and its ultimate fate depends on a number of complex factors, the understanding of the radionuclide behavior and its distribution in the environment is of great importance. In this paper ^{232}Th and ^{228}Th concentrations in Santos and São Vicente estuary sediments are presented. The relations between the content of organic matter, silt and clay and Th-isotopes amount are also discussed.

2. THE STUDY AREA

Santos Basin, located in Southwest Brazil, São Paulo State, comprising the counties of Santos (725 km^2), São Vicente (131 km^2) and Cubatão (160 km^2), is considered the most important industrial region of the country. These man-made activities, on the other hand, represent a potential threat to the surrounding environment [7, 8, 9]. Its estuarine system is responsible for the catchment and deposition of a considerable amount of material loaded by rivers, such as major and traces metals and other pollutants discharged by the local industrial activity.

Figure 1 shows the study area and the sampling location. For a better understanding of the results, the region was divided in rivers (identified by R), Santos Channel (CS), São Vicente Channel (SV) and Santos Bay (B). The rivers samples were divided into RC-samples, which represent sediments from Cubatão River; RM-samples, which represent sediments from Mogi River and R-samples, which represent sediments from others estuarine rivers that are subjected to tidal effects, and therefore possess salinity values bigger than the former rivers. In Santos and São Vicente Channel the salinity range from 0.5 to 35 and Santos Bay possess salinity of 35. In the surrounding of Cubatão and Mogi rivers are located a large number of industries, including phosphate fertilizer plants. In Santos Channel is located the most important Brazilian harbor.

3. MATERIALS AND METHODS

Samples were collected in 1999 in Santos and São Vicente estuary with a Van Veen grab and in 2002 in Cubatão and Mogi Rivers using PVC core with 20cm of length and 4cm diameter. Samples were maintained under 4ºC before laboratory treatment. Samples were dried at temperature of 65ºC till constant weigh and sieved to a grain size of 150 mesh. Part of the sample was packed in plastic vessels for gamma spectrometry for the determination of ^{228}Th and approximately 150mg were used for ^{232}Th measurement by neutron activation analysis. Both techniques are described in Mazzilli *et al.* [3].

4. RESULTS AND DISCUSSION

Table I shows the activity concentration of ^{232}Th and ^{228}Th and activity ratio ^{228}Th/^{232}Th. Considering all samples, ^{232}Th concentration presented a range of 6.5 to 198 Bq kg^{-1}, with mean value of 57±39Bq kg^{-1}, for N=42 and ^{228}Th varied from 12 to 110Bq kg^{-1}, with a mean value of 74±23Bq kg^{-1}, for N=18. Figure 2 shows the mean activity concentration for ^{232}Th normalized with Post Archean Australian Shale (PAAS – [10]) in the six compartments studied. The normalization with PAAS has the advantage of minimize mineralogical and grain size effects. It can be seen that the amount of ^{232}Th is higher in Mogi and Cubatão Rivers and decreases in the estuarine system, where salinity rises, suggesting that the main source for this nuclide are terrigenous and detrital materials. Nevertheless, some points deserve special attention. Point sampling RM0 (figure 2) is located in a small stream, tributary of Mogi River, and is close to phosphogypsym piles, a by product of fertilizer industries. It is known that in the fertilizer Brazilian production 80% of ^{232}Th is transferred to phosphogypsum [11].

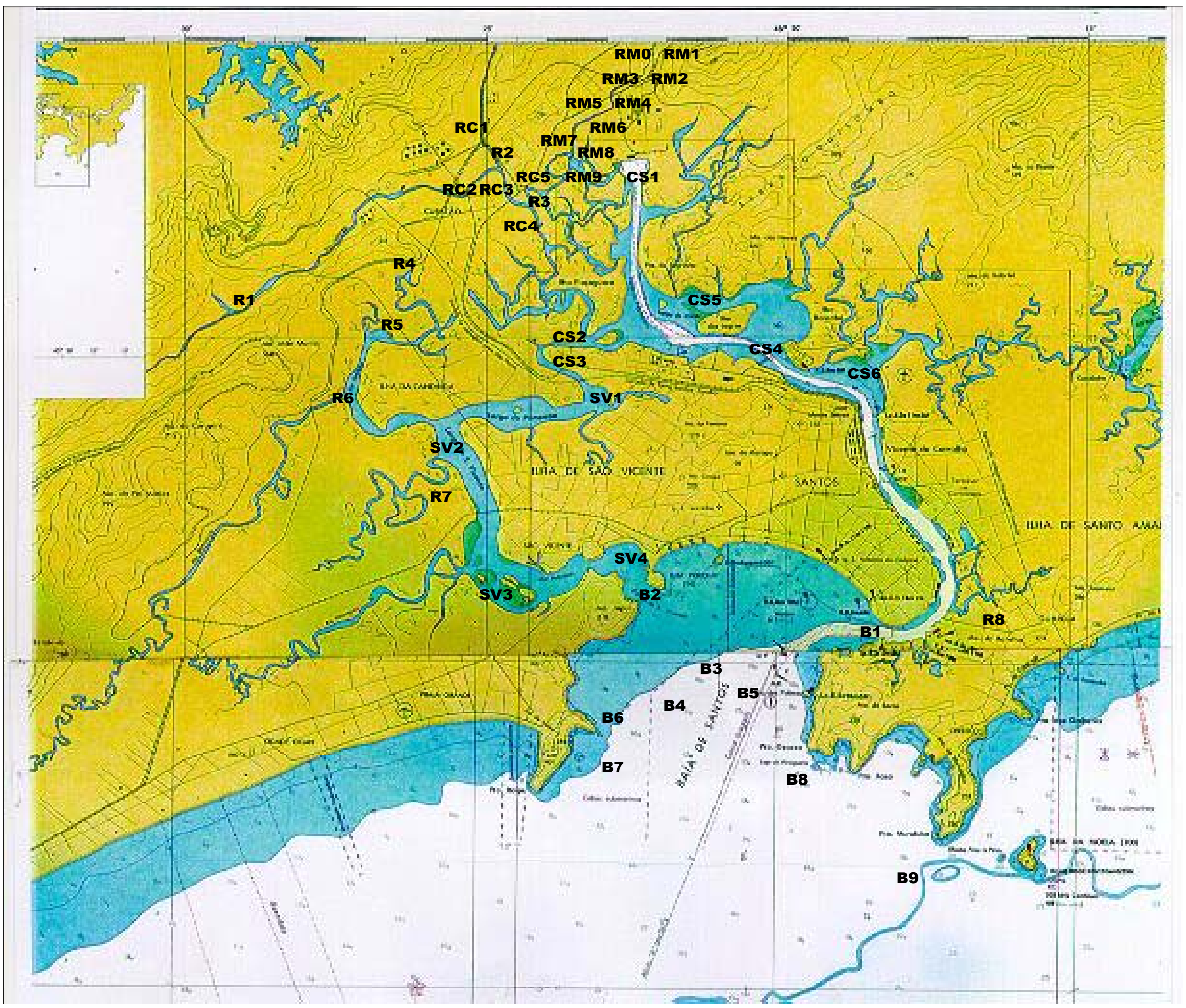

Figure 1. Study area showing the sampling location

The activity concentration obtained for this point clearly shows an anthropogenic contribution to the amount of ^{232}Th in the sediment. An enhancement of thorium in sediments in the vicinity of phosphogypsum piles was also determined by [12], which also showed that the main process scavenging Th from the solution is its incorporation in amorphous ferromanganese oxihidroxides. As seen, due to its geochemistry behavior in these environments, an input of thorium from external sources will rapidly incorporate to the sediment by precipitation processes.

Points B1, B3 and B9 strongly contribute to the enhancement of Th activity concentrations in the mean value of Santos Bay sediments. Point B1 is located in the mouth of Santos Channel, point B3 is located near a submarine sewage and point B9 is located in an ancient deposit of sediment dragged from Santos Channel due to the Santos Harbor. Although Th is quite insoluble, sediment remobilization due to man-made activities can promote alteration in its distribution in the environment.

The mean activity concentration for ^{228}Th (figure 2) presents the same trend as ^{232}Th, although it has been determined only in Cubatão and Mogi Rivers and Santos Channel. It is generally accepted that the main source of ^{228}Th in marine sediment is its authigenic production from ^{228}Ra due to their short half-lives (1.9 and 5.75yr, respectively). Nevertheless, in the near shore environment desorption of Ra seems more efficient diminishing the ^{228}Th in superficial sediments.

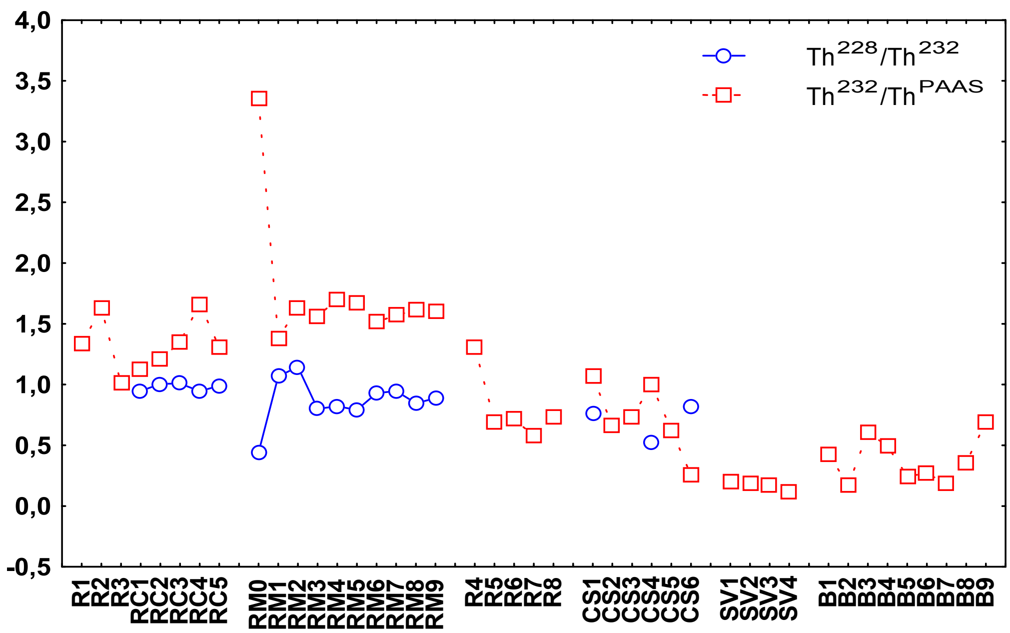

Figure 2. Activity ratio ^{228}Th/^{232}Th and ratio between ^{232}Th and its content in PAAS

Figures 2 and 3 show the ^{228}Th mean activity, ^{228}Th/^{232}Th mean activity ratio and ^{232}Th/Th_{PAAS} mean activity ratio, respectively, for Cubatão and Mogi Rivers and Santos Channel. It can be seen that Cubatão River present values closer to unit for these ratios than the other compartments and that the mean activity tends to decrease from river samples to bay samples. These results can be explained by desorption of radium as salinity increases [13]. Desorption of Ra could, therefore, give rise to ^{228}Th far away from external sources of thorium other than the natural weathering. Thus desorption/adsorption processes can explain the very low value for the activity ratio found in point RM0, as well as the higher value found in point RM2, once the latter is located immediately before a barrage, in Mogi River. After the barrage, in point RM3, the activity ratio value fell dawn and start to raise downstream Mogi River reflecting the influence of ^{228}Ra content in the sediment.

Table I. Activity concentration of ^{232}Th and ^{228}Th, in Bq kg^{-1} and activity ratio ^{228}Th/^{232}Th

	^{232}Th	^{228}Th	^{228}Th/^{232}Th		^{232}Th	^{228}Th	^{228}Th/^{232}Th
CS1	63±3	48±5	0,76±0,08	R4	77±4		
CS2	39±2			R5	41±2		
CS3	44±2			R6	42±2		
CS4	59±3	31±2	0,52±0,04	R7	34±2		
CS5	37±2			R8	44±4		
CS6	15,1±0,8	12±1	0,82±0,11	R1	79±4		
SV1	11,5±0,5			R2	96±5		
SV2	10,9±0,5			R3	60±3		
SV3	10,2±0,4			RC1	66±3	63±6	0,9±0,1
SV4	6,6±0,3			RC2	71±3	72±6	1,0±0,1
B1	25±1			RC3	80±4	80±7	1,0±0,1
B2	9,9±0,5			RC4	98±5	93±8	0,94±0,09
B3	36±2			RC5	77±4	76±7	1,0±0,1
B4	29±1			RM0	198±9	87±8	0,44±0,04
B5	14,6±0,6			RM1	82±4	87±8	1,1±0,1
B6	15,8±0,7			RM2	96±5	110±11	1,1±0,1
B7	11,0±0,4			RM3	92±4	74±7	0,80±0,08
B8	21,2±0,8			RM4	100±5	83±7	0,82±0,08
B9	41±2			RM5	99±5	78±7	0,79±0,08
				RM6	89±4	83±7	0,93±0,09
				RM7	93±4	88±11	0,9±0,1
				RM8	95±4	81±7	0,85±0,09
				RM9	95±4	84±8	0,89±0,09

Figure 4 shows the relation between the activity concentration of ^{232}Th and ^{228}Th and the content of organic matter, silt and clay for Cubatão and Mogi Rivers samples. In Cubatão River sediment samples both Th-isotopes decrease with the increase of either organic matter, or silt and clay. In Mogi River sediment samples the distribution of both nuclides are very uniform except in point RM0 for ^{232}Th and point RM2 for ^{228}Th and the regression curve obtained was obviously influenced by these points. The content of Th-isotopes reflects the sediment mineralogy [14] and and is weakly correlated with organic matter [12] being associated with the residual fraction. Therefore, higher amounts of organic matter can reflect in the decrease in total concentration of thorium, as seen in Cubatão River.

Considering Th as a lithogenic element associated with heavy minerals one must expect that as the sediment becomes finer thorium concentration must diminishes once silt and clay are mainly formed by light minerals, generally feldspar associated with K.

From the above considerations it is clear that points RM0 and RM2 are affected by the phosphate plant activities and the effect of a ^{232}Th and ^{228}Th liberation in the environment act in a short range of the release point.

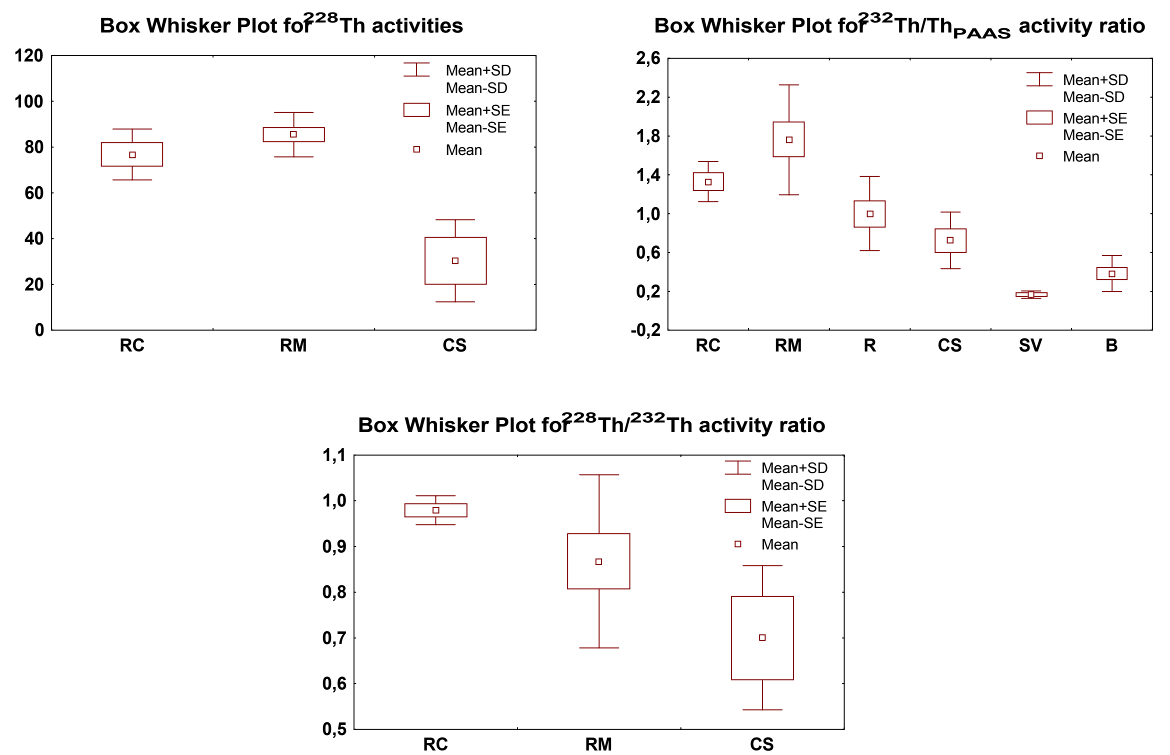

Figure 3. ^{228}Th mean activity, in Bq kg^{-1}, ^{228}Th/^{232}Th mean activity ratio and ^{232}Th/Th$_{PAAS}$ mean activity ratio

5. CONCLUSIONS

The activity concentration of ^{232}Th and ^{228}Th presented a mean value of 57±39 Bq kg^{-1} and 74±23 Bq kg^{-1}, respectively in samples from Santos and São Vicente Estuary and Santos Bay. The general patter of thorium distribution follows the order: river > estuary > bay.

Although the input of terrigenous and detrital materials, originated in weathering processes, seems to be the main responsible for Th-isotopes concentration in the sediment, man-made activities also contribute to the total amount of these nuclides. This influence can be seen in points RM0, RM2 and in points located in Santos Bay which are related to anthropogenic activities (B1, B3 and B9).

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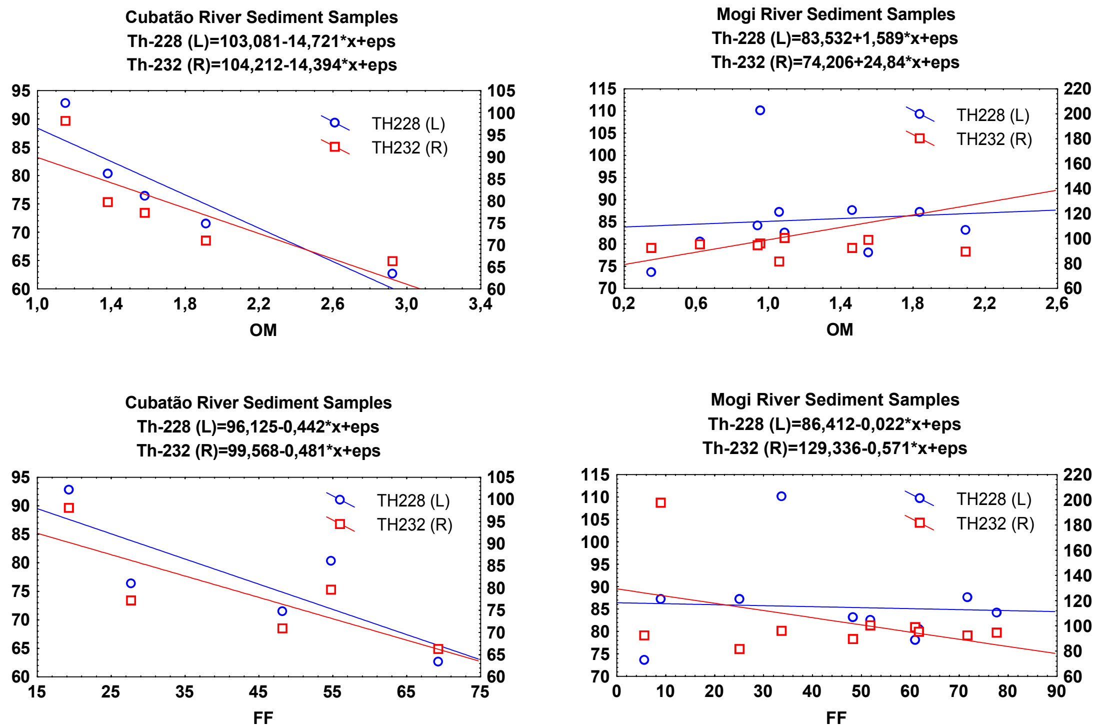

Figure 4. Regression lines for Th isotopes against organic matter (OM) and silt plus clay (FF).

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